SELF-DIFFUSION PHENOMENA

IN ZINC AMALGAMS

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SELF-DIFFUSION PHENOMENA

IN ZINC AMALGAMS

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SUMMARY

Self-diffusion coefficients for 1.440 weight percent zinc amalgams were measured at 323, 373, 423, and 473°K and atmospheric pressure using the modified shear-cell technique developed by Broome and Walls. These values are in fair agreement with the values determined by Schadler and Grace and by Walls who used the capillary-reservoir technique. The data were fitted to an Arrhenius type equation giving:

$$D = 4.6 \times 10^{-4} \exp(-1920/RT)$$

where D is in cm^2/sec.

The inter-diffusion coefficient for the system was calculated from the Darken equation and the self-diffusion coefficient from the Walls-Upthegrove Equation.

CHAPTER I

INTRODUCTION

The measurement of properties of liquids has been an activity of continuing importance from two standpoints, viz., to support technological demands and to enhance the fundamental understanding of the liquid state by providing data suitable for validation of proposed theory. Moreover, the availability of sufficient data to indicate functional relationships sometimes suggests patterns for theoretical innovation. Continued development of theory has led to many situations in which there is less disagreement among different theoretical models for diffusion behavior than the disagreement in experimental data available from various sources. These circumstances are true for diffusion measurements in liquids, and it emphasizes the pronounced need for futher refinement of the experimental methods.

There has been an interest in liquid metals diffusion phenomena for more than two centuries, and since 1850, numerous attempts have been made, using a variety of experimental techniques, to measure diffusion coefficients in liquid metals. However, these efforts have been only moderately successful in yielding data from which diffusion coefficients may be calculated with accuracy. In fact, a precision of $\pm 10\%$ is considered quite good for measurements with liquid metal systems. Greater precision is currently obtainable for aqueous or organic systems because of the availability of accurate methods for determining concentrations and

because surface tension effects are less pronounced.

Extensive reviews of diffusion mechanisms and diffusion data have been published (1,2,3). The comprehensive tabulation of mutual diffusion coefficients presented by Edwards et al. (3) is a useful source of information and a guide to those systems for which data are available.

This research is an attempt to add to the understanding of the liquid state by extending the modified shear-cell method to include the measurement of liquid self-diffusion coefficients in amalgams. The reliability of this method has been demonstrated by Broome and Walls (4,5) and by Barras, Walls, and Hines (6). A zinc amalgam was selected because zinc-mercury is one of the iso-viscous pairs (7) and data obtained by using the capillary-reservoir technique are available for comparison with data taken using the shear-cell method.

CHAPTER II

DIFFUSION PHENOMENA

Definition and Significance of Diffusion Coefficients

Diffusion theory proceeds from the basic law that the rate of mass transferred by diffusion with respect to time per unit area is directly proportional to the rate of change of concentration with distance in the direction of flow, i.e.:

$$J = -D\frac{dC}{dX} \tag{1}$$

where:

J = flux relative to the mass average velocity, gm-mole/cm^2sec

C = concentration of diffusing species , gm-mole/cm^3

X = position along the concentration gradient, cm

D = diffusion coefficient, cm^2/sec

This equation, usually referred to as Fick's first law, defines the diffusion coefficient as the proportionality constant between the diffusive flux and the concentration gradient. The negative sign arises because diffusion occurs in the direction of decreasing concentration.

Fick's second law is obtained from Equation 1 and the continuity equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial X^2} \qquad (2)$$

where:

t = time of diffusion, sec.

The solution to Fick's second law for the diffusion system used in this work is presented in Appendix C. The assumptions embodied in Fick's second law as given by Equation 2 are: D is constant and independent of concentration and a concentration gradient exists only along the X-axis. Temperature gradients, pressure gradients, and external forces also contribute to the diffusion flux, although their effects are negligible in this work.

The development of these equations is entirely phenomenalogical and takes no account of atomistic considerations. For example, consider a plane surface within a system. An individual atom in this system can move in any direction with equal probability. If the atoms in the system are indistinguishable, the net flow of atoms across this plane due to the random thermal motion of the atoms will be zero. Thus, in the absence of concentration gradients the net flux is zero and Equation 1 is satisfied. For the case where a system contains two distinguishable species, A and B, with different concentrations on opposite sides of the plane, the motion of the individual atoms of A and B is assumed to be random, so that any given atom has an equal probability of moving in any direction. The flux of type A atoms crossing the plane in one direction will be equal to the product of the probability that an atom will move in that direction times the concentration

of A atoms on the side from which the particular atom is leaving. Type A atoms will cross the plane in both directions, but since there are more A atoms on one side than on the other, there will be a net transfer of A atoms from the higher concentration to the lower concentration. Moreover, if the bulk system is to be static there must be a net flux of B atoms in the direction opposite to the A atoms. The self-diffusion coefficient may be thought of as a measure of the frictional forces that exist between the atoms as a result of their relative motion. In this sense, the diffusion coefficient is analogous to the viscosity, μ, defined as the proportionality factor between momentum flux and velocity gradient as given in Newton's law of viscosity:

$$\tau = -\mu \frac{dv}{dX} \tag{3}$$

where:

τ = the shear stress exerted in the direction of fluid flow on a surface perpendicular to that flow, dynes/cm^2

v = velocity of fluid flow, cm/sec

X = direction of fluid flow, cm.

The diffusion coefficient is also analogous to the thermal conductivity, k, defined as the proportionality factor between the heat flux and temperature gradient in Fourier's law of heat conduction:

$$q = -k \frac{dT}{dX} \tag{4}$$

where:

q = heat flow per unit area, cal/sec cm^2

T = temperature, °K

X = direction of heat flow, cm.

Fick first recognized this analogy between diffusion and heat conduction in formulating Equation 1.

The assumption made above was that A and B have similar interatomic forces, i.e., the force pairs, A-A, A-B, and B-B are indistinguishable. This is the normal assumption made in determining the self-diffusion coefficient of an element using radioisotopes of that element. Generally this assumption is not good where the species have different chemical properties. When the force pairs are not similar and there is a concentration gradient in the system, the individual atoms will not have an equal probability of moving in any direction. Instead, certain atomic configurations will be favored and will result in a net transfer of A atoms somewhat different than the transfer of B atoms. Herein lies the basic difference between the phenomenon of self-diffusion and inter-diffusion. Due to the presence of a concentration gradient of chemically distinguishable atoms perturbing the motion of the atoms, the movement of inter-diffusing atoms is not random in the same sense that it is for self-diffusing atoms.

Self-diffusion coefficients may be measured in a system without the presence of a gradient in chemical concentration by observing the movement of radioactive tracers. Inter-diffusion, sometimes referred to as chemical or mutual diffusion, implies the presence of a concentration gradient. Self-diffusion includes not only diffusion of solvent atoms in a pure solvent such as ^{110}Ag in pure Ag, but also solute atoms in trace quantities in a solvent, e.g., ^{198}Au at infinite dilution in pure Ag. It also occurs between two binary amalgams of the same composition

when one of the elements of one amalgam is tagged with a tracer.

Experimental Methods

Most of the self-diffusion data in liquid metals have been obtained by using radioactive tracers in conjunction with some form of confining capillary. The available techniques have been summarized by Walls (1) and by Edwards et al. (3). The capillary-reservoir technique is currently the most popular method for making liquid metal diffusion studies. The diffusion system used in this work is a compromise between the long-capillary technique and other shear-cell methods.

The use of radioactive tracers in conjunction with the capillary-reservoir technique, as described by Anderson and Saddington (8), offers experimental simplicity relative to other methods and has been employed for high temperature measurements. In this method, a capillary with one end closed is filled with a radioactively labeled liquid metal and immersed in a large bath of liquid metal having a different isotopic composition. The capillaries are normally about 1 mm in diameter and a few centimeters long. After a measured time the capillary is removed from the bath, and the composition of the material in the capillary is determined and compared with the initial composition of metal in this capillary. The diffusion coefficient is determined from this information.

The boundary conditions for the solution to Fick's second law in this instance are:

$$\frac{\partial C(0,t)}{\partial X} = 0 \quad \text{for} \quad t > 0 \tag{5}$$

$$C(L,t) = C_r \quad \text{for} \quad t > 0 \tag{6}$$

$$C(X,0) = C_o \quad \text{for} \quad 0 < X < L \tag{7}$$

where:

C = concentration, cpm

L = capillary length, cm

X = distance measured from the closed end of the capillary, cm

t = time of diffusion, sec

D = diffusion coefficient, cm^2/sec

C_r = reservoir concentration, cpm

C_o = initial uniform capillary concentration, cpm

The integrated solution in dimensionless form is:

$$\psi = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left[-\frac{(2n-1)\pi}{2}\right]^2 \theta \tag{8}$$

where:

$$\psi = \frac{C_f - C_r}{C_o - C_r} \tag{9}$$

$$\theta = \frac{Dt}{L^2} \tag{10}$$

and C_f = average final concentration in the capillary, cpm.

The capillary-reservoir technique permits several capillaries to be immersed simultaneously in the reservoir, thus reducing the time required to obtain data. The method, however, is subject to a number of errors that are difficult either to eliminate experimentally or to account for in the mathematical formulation of the problem. The boundary condition expressed in Equation 7 is not met when the capillary is immersed in

the reservoir, due to turbulent mixing at the mouth of the capillary caused by surface tension. Moreover, the relative motion between the capillary and the reservoir, which is needed to maintain the boundary conditions expressed in Equation 6, may also cause turbulent mixing in the mouth of the capillary. All of these effects tend to increase the diffusion coefficient. Although the precision may be good, the uncertainties due to hydrodynamic effects limit the absolute accuracy to about 10%.

The long-capillary method described by Carreri, Paolotti, and their coworkers (9,10,11,12,13), has been used successfully in many liquid metal systems. This technique involves filling one half of a long capillary (150 to 200 mm in length) with a material of one concentration and the other half with material of a different concentration. After a diffusion run, the capillary is sectioned and the concentration profile is determined.

This method reduces the convection effect found in the capillary-reservoir technique and allows the study of metals with high melting points. This method also allows the measurement of the concentration profile which can not be obtained from the capillary-reservoir system. However, serious experimental errors may be introduced due to the melting, expansion, and contraction of the diffusion couple during a diffusion run.

The shear-cell technique, as originally developed, consists of several discs mounted coaxially. Off center holes are drilled in these discs such that they may be aligned to form the diffusion path. The metals of different compositions are kept separated until the run is begun by aligning the holes that make up the diffusion path. After the diffusion run, the segments are sheared, breaking the diffusion

capillary into as many parts as there are segments. The diffusion coefficient is obtained from the slope of the concentration gradient calculated from the alloy composition in each compartment.

The principal disadvantage of this technique is that stirring may possibly occur when the discs are rotated at the conclusion of the experiment. The magnitude of this mixing is dependent on the length to diameter ratio of each of the compartments with the larger ratio producing less mixing. This method, like the capillary-reservoir technique, keeps the two liquid metals separated until the actual diffusion run is started. Unlike the long-capillary method, there is no premature contacting of the phases with the attendant uncertainty in the time or temperature of the run.

Review of Experimental Data

Wilson (2) has reviewed the literature pertaining to liquid metal diffusion coefficients. He concludes that self-diffusion data are often subject to an error of $\pm$50%, while in alloys the diffusion coefficients may be in error by as much as 100%. Edwards et al. (3) have also presented a comprehensive review of diffusion coefficients for liquid metal systems. They undertook a critical review of the available literature and attempted to ascertain the reliability of existing data. They state that some of the experimental data are quite trustworthy, while for other measurements, an estimate of $\pm$100% would be conservative.

Self-diffusion studies have been reported for pure mercury by several investigators (4,14,15,16,17,18,19). The mercury diffusion data reported by Broome (4) and by Meyer (17) probably represent the best

values and are in excellent agreement over a wide temperature range with the data of Nachtrieb and Petit (16) and Hoffman (19). Broome utilized the modified shear-cell method and reported diffusion coefficients from 248°K to 524°K. Meyer measured the self-diffusion coefficients of liquid mercury using the capillary-reservoir technique over the temperature range 273°K to 512°K.

Concentration gradients of the bulk material, which promote convection, are absent in self-diffusion measurements. However, the diffusion coefficients have been found to vary with the capillary diameter and with the material from which the capillary is made. Small effects like these are masked in the study of inter-diffusion by such gross effects as volume changes occurring during the diffusion run and the presence of concentration gradients.

Self-diffusion measurements in amalgams have been made by several investigators (18,20,21,22). Self-diffusion of one component in an amalgam may be measured by bringing into contact two alloys of identical composition. One of these alloys, however, contains radioisotopes of the metal whose self-diffusion coefficients are to be studied. The other amalgam is prepared from inactive metals.

Schadler and Grace (18) obtained self-diffusion coefficients for zinc amalgams at several compositions over the temperature range 273°K to 333°K, using the capillary-reservoir technique. The authors used their data to verify the applicability of Darken's (23) relationship between self and inter-diffusion coefficients.

Walls (20) also determined self-diffusion coefficients for zinc and cadmium in zinc and cadmium amalgams using the capillary-reservoir

technique. The zinc data, taken at several compositions over the temperature range 323°K to 392°K, is in excellent agreement with the data of Schadler and Grace. However, there is considerable scatter in the cadmium data, with some data exhibiting an inverse temperature behavior.

Foley and Liu (21) determined the self-diffusion coefficients for thallium in thallium amalgams at 298°K for 8 compositions using the capillary-reservoir technique. Castleman and Conti (22) have determined self-diffusion coefficients for gold and silver in gold and silver amalgams respectively over the temperature range 298°K to 342°K using the capillary-reservoir technique.

A great deal of data has been published for inter-diffusion in amalgams. Von Wogau (24) used the shear-cell technique to determine the diffusion coefficients of lithium, sodium, potassium, rubidium, cesium, calcium, strontium, and barium in their respective amalgams at low temperature. Diffusion coefficients for tin and bismuth in their amalgams were derived from polarographic data by Cooper and Furman (25). An electrolysis cell, using a thin ribbon-shaped capillary, has been used by Mangelsdorf (26) to study cadmium amalgams from 298°K to 423°K. Von Meyer (27) also used the shear-cell technique to determine the diffusion coefficients of zinc, cadmium, and lead in amalgams at low temperatures. A dropping-amalgam electrode was used by Stackelberg and Toome (28) to obtain the diffusion coefficients for cadmium, indium, lead, and sodium amalgams at 295°K. Cadmium amalgams were studied by Cohen and Bruins (29) and by Turner and Winkler (30). Furman and Cooper (31) studied the polarographic behavior of amalgams of zinc, cadmium, thallium, lead, and copper and from this they calculated values for the diffusion

coefficients. By measuring the electrical resistivity of potassium-mercury systems the diffusivity was determined over the temperature range 589°K to 811°K and from 0 to 0.7 mole fraction by Bonilla, Do-ik Lee, and Foley (32). Edwards et al. (33) have developed an experimental method to measure binary liquid metal diffusion coefficients with a concentration cell. They report diffusion coefficients for potassium-mercury, sodium-lead, and sodium-tin from 500°K to 900°K. Using the capillary-reservoir technique, the inter-diffusion coefficient for thallium in thallium amalgams was measured by Foley and Reid (34). Weischedel (35) measured the inter-diffusion coefficient for zinc and cadmium amalgams at low temperatures. The diffusion of lead and mercury has been measured by Warburton (36) in lead-mercury alloys containing up to 8 atomic percent mercury between 473°K and 573°K using the serial-sectioning technique. Raudel and Moshkevich (37) report values of the diffusion coefficients of lead and zinc in dilute amalgams from 273°K to 323°K using the method of truncated capillaries.

Theoretical Models

Many theories have been published which attempt to predict the diffusion behavior of a liquid. Since these are summarized elsewhere (1,3), this work will not attempt to discuss these models. Only the two relationships used in correlating the data obtained in this work will be presented.

Darken (23) has related diffusion coefficients measured by using radioactive tracers to the inter-diffusion coefficient in terms of the thermodynamic properties of the system. His relationship is:

$$D = (N_A D_B + N_B D_A)\ (1 + N_B \frac{d\ \ell n\ \gamma_B}{dN_B}) \qquad (11)$$

D = inter-diffusion coefficient, cm^2/sec

N_A = atomic fraction of A

N_B = atomic fraction of B

γ_B = activity coefficient of B

D_A = self-diffusion coefficient of A, cm^2/sec

D_B = self-diffusion coefficient of B, cm^2/sec

Walls and Upthegrove (38) have developed a model for self-diffusion in liquids which leads to the following equation:

$$D = \frac{KT\ \gamma^{-1/3}}{2\pi\ h\ b\ (2b+1)} \left(\frac{V}{N_o}\right)^{2/3} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \qquad (12)$$

D = the self-diffusion coefficient, cm^2/sec

K = Boltzmann constant, erg/°K

T = absolute temperature, °K

γ = configurational parameter dependent only upon the coordination number of the liquid

h = Planck's constant, erg/sec

b = geometrical parameter which is defined as the ratio of the diffusing particle radius to the interatomic spacing

V = molar volume, cm^3/gm-mole

N_o = Avogadro's number, $(gm\text{-}mole)^{-1}$

ΔS^* = entropy of activation for kinematic viscosity, cal/gm-mole °K

ΔH^* = enthalpy of activation for kinematic viscosity, cal/gm-mole

This equation contains three parameters: a configurational constant which can be calculated from the coordination number, the entropy and enthalpy of activation which can be determined from kinematic viscosity,

and the parameter, b, obtained by fitting diffusion data to Equation 12.

CHAPTER III

INSTRUMENTATION AND EQUIPMENT

Diffusion Cells

The diffusion cells, as described by Broome and Walls (4,5), were used in this work. The modified shear-cell used by Broome and Walls is a compromise between other shear-cell methods and the long-capillary design. The better parts of both techniques, as described in Chapter II, are retained, and many of the problems which resulted in experimental and mathematical difficulties are eliminated.

The cell consists of two segments; one is firmly attached to a base plate and the other segment slides along the base plate. It is this relative motion between the two segments that forms or shears the diffusion capillary. One of the capillaries is filled with radioactive material while the other is filled with inert metal. The diffusion coefficient can be determined from measurements of the net exchange of radioisotope between the two segments of the capillary column.

Several sets of matched cells were used in this work. Two sets had capillary diameters of approximately 1.2 mm and the other set had diameters of 2.6 mm. All capillaries were a little over 30 mm long. A large diameter stopcock (158 mm) at the rear of the capillary is used for filling the capillary. When in the closed position, the large diameter provides an essentially flat end to the capillary.

Overflow tubes are provided such that a capillary is extended

into the other segment. These tubes are located so that the capillary and its overflow can be simultaneously aligned. Because expansion takes place in the overflow tubes; the expansion problem encountered with the long-capillary method is avoided. The two diffusion capillaries never come in contact until the entire system is at the diffusion temperature. Once a capillary and its overflow are sheared, the overflow is isolated and never comes in contact with the diffusion couple. Provision of these overflow tubes aids in initially filling the capillaries and also serves to equalize the pressure between the two sections of the capillary column and the environment at the diffusion temperature. Without overflow tubes, the high surface tension of the liquid metal would make complete filling of the capillary very difficult. This could result in necking of the liquid thread at the shear interface. Likewise, the cutting of the thread by the stopcock avoids trapping gas which would expand upon heating.

A drive motor is attached to the movable cell via a push rod. A mechanical stop is placed on the base plate such that the drive motor is stalled when the movable segment slides into the proper horizontal alignment. The cell segments are mounted on the base plate with spring loaded screws, thus assuring vertical alignment. A spring loaded bar placed at the rear of the movable segment assures sealing at the shear interface.

Materials selected for fabrication of the cells were compatible with the liquid metal at high temperature, were machineable, and could take a very smooth finish. For this work, the base plate and drive assembly were made of low carbon steel. Cell segments were also made

of low carbon steel, but the stopcocks were made of hardened drill rod. The stopcock was fabricated from material of a greater hardness to preserve the surface finish in the hole and on the stopcock.

Ovens

The diffusion runs took place in specially constructed laboratory ovens. Two ovens were used to speed the data taking. Both ovens maintained the temperature to within $\pm 0.5^{\circ}C$ of the control setting. The temperatures were measured with a calibrated iron-constantan thermocouple using a Leeds & Northrup 8686 millivolt potentiometer. As a check, temperatures were also measured with a calibrated thermometer. A Honeywell Electronik 193 strip-chart recorder was used to monitor the temperature variation during the diffusion runs.

One oven was constructed of 1" Marinite. The Marinite oven was controlled by a Fisher Proportional Temperature Controller. Heat in the oven was supplied by two 675 watt flat heating elements wired in parallel.

The other oven was built from Transite and firebrick. The schematic of the heating elements is shown in Figure 1. The ballast heater circuit employed a powerstat variable transformer type 3PN1178 as the voltage regulator. The powerstat was adjusted until the ballast heater supplied 60 to 80% of the heat required by the oven. The remaining heat was supplied by two heating elements controlled by a Honeywell R7291A 1026 SCR Power Module 120 volt unit, coupled with a R7355C 1082 3 mode controller with current output. The sensor for the unit was a 3B10P12-1A type (J) thermocouple assembly.

A Precision Scientific Model 524 vacuum oven was used to degas the mercury samples contained in the diffusion cells prior to placing them in the ovens.

Stock Materials

The mercury used in the diffusion measurements was triple distilled Caulk 20th Century mercury with a non-volatile residue of less than 5ppm and the zinc used was obtained from K&K Laboratories Inc. with a purity of 99.9998%. New England Nuclear supplied the radioisotope, zinc-65, in the form of $ZnCl_2$. The table of specifications for the zinc-65 is found in Appendix B.

Power Packs and Electroplating Equipment

The current source used in this experiment to electroplate zinc-65 onto inert zinc was a Hewlett Packard Model 721A power supply. It was also used to furnish current to hold the amalgams in solution, as will be described in the procedure section. The other power supply was an Electronic Measurements Co. Model TR018-1. Twelve volt lantern batteries were also used to hold the amalgams in solution.

The plating solution was made up by dissolving 59.17 gms of NaCl, 38.58 gms of $ZnCl_2$, and 5.31 gms of $AlCl_3 \cdot 6H_2O$ in distilled water in a 250 ml volumetric flask.

Counting Equipment

The radioactive counts were measured on a Nuclear-Chicago Mark I liquid scintillation counter. The amalgam samples to be counted were collected in 20 ml liquid scintillation counting vials and 20 ml of

acid was pipeted into them. The acid was a 50/50 mixture of nitric acid and distilled water. A large volume of this solution was prepared at the beginning of the experiment and used throughout the course of the work.

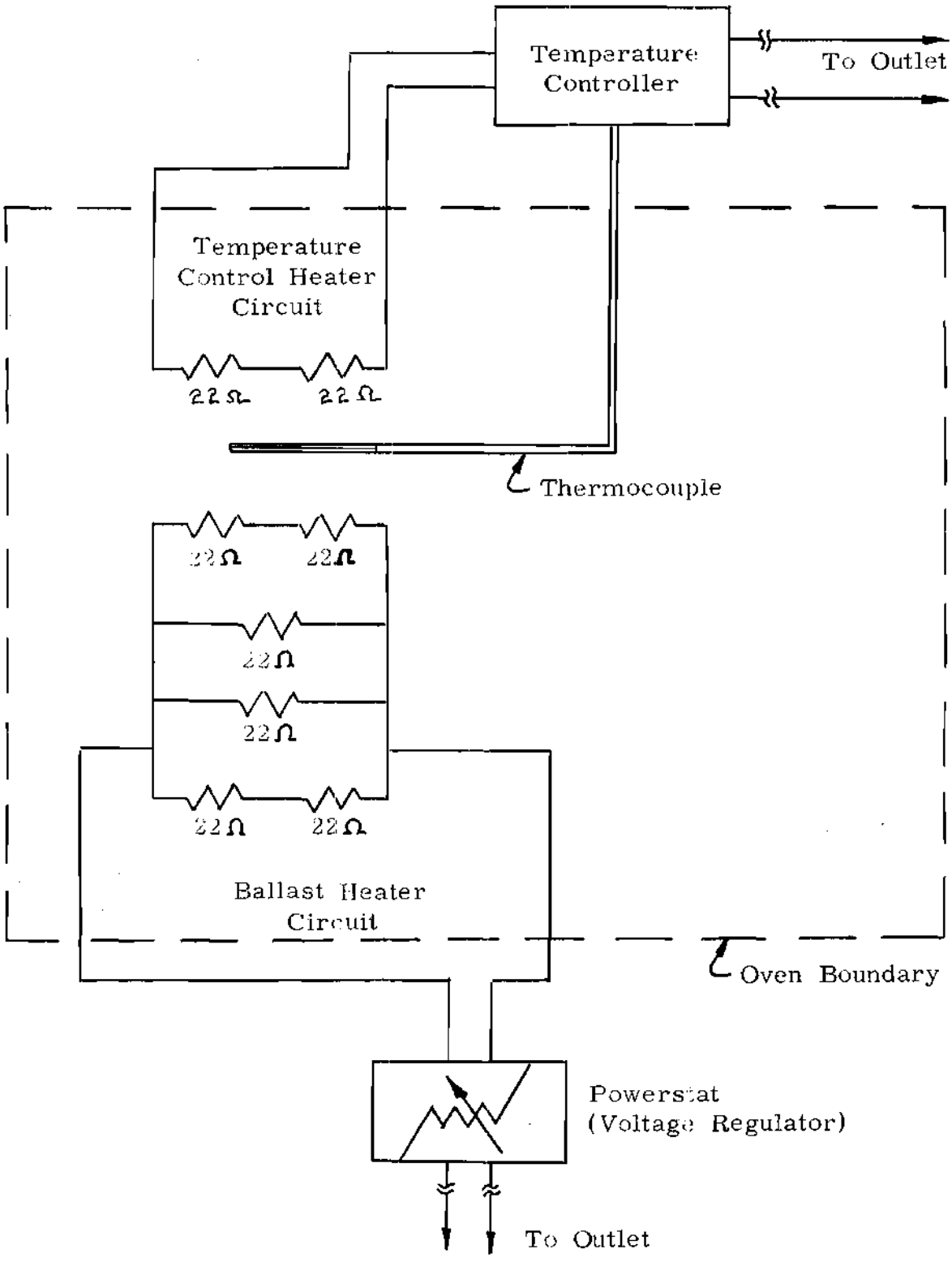

Figure 1. Schematic of Diffusion Oven Heating Elements

CHAPTER IV

PROCEDURE

The amalgams used in this work were prepared by dissolving the solute zinc directly into the mercury. The technique of Crenshaw (39) was employed, in which the mercury is made the cathode of a cell and a platinum anode is placed in distilled water over the mercury. The solute material was placed on the mercury surface and a 12 volt potential was applied to the cell to enhance the amalgam formation. It was necessary to store the amalgams in this manner to prevent preferrential oxidation of the zinc. Current flow was usually less than 0.5 ma and was measured using the Hewlett Packard 721A. When the power supplies were needed to plate the radioisotopes onto the inert zinc, a 12 volt lantern battery was used to hold the amalgam in solution. It took 10 to 20 hours for the zinc to dissolve in the mercury, depending on whether the cells were heated with a heating tape.

The radioactive amalgams were prepared by two methods, one involving irradiating zinc in the reactor at the Frank H. Neely Nuclear Research Center at the Georgia Institute of Technology.

The other method involved electroplating zinc-65 purchased from New England Nuclear onto the zinc; the method of Thompson (40) was used as a guide in the electroplating procedure. A length of 22 gauge platinum wire, bent to provide it more surface area, was used as the anode. Ten ml of the plating solution described in the equipment section was pipetted into a 50 ml beaker. The zinc-65 solution was diluted to

10 ml in a 10 ml volumetric flask and half of this solution was added to the beaker. A piece of inert zinc, which had been cleaned in HCl, was used as the cathode. After plating for 24 hours at 15 ma, using the Hewlett Packard 721A as the power source, the cathode was removed and dissolved in the mercury as described above. Using this method, several hundred microcuries of zinc-65 could be electroplated onto the inert zinc and this zinc could be used to make up approximately 200 gms of amalgam.

The other method of producing radioisotopes was to place 2 gms of inert zinc in the nuclear reactor for 2 hours. The disadvantage in this method is that in addition to the desired radioisotope, zinc-65, several other short lived isotopes were produced. Zinc-69 and zinc-69_m were the major short lived isotopes with half lives of 57 minutes and 36.9 hours respectively. The majority of the runs in this work were made with the electroplated radioisotopes.

Prior to a diffusion run the shear cells were cleaned, dried, and lubricated. After the diffusion cells were emptied following a diffusion run, radiation contamination could not be detected. Alignment of the capillary was carefully checked after the cells were assembled and before they were filled with the diffusing materials. The amalgams were then loaded into the cell capillaries and aligned with the capillary overflow tubes to insure that the capillary sections would be completely filled. The cells were then placed in the vacuum oven at 403°K and 380 mm mercury for 6 hours to outgas the amalgams. After the shear cell assembly had been removed from the vacuum oven and allowed to cool for about 1 hour, the stopcocks were rotated and the excess mercury in the

filling ports was drained off. About 12 gms were required for the diffusion measurement in the cells with the larger diameter capillaries and about 6 gms were used in the cells with the smaller capillaries.

The assembled diffusion cells with the capillary sections containing the diffusion material were placed into the ovens and leveled. The temperature controlled oven was then turned on. When the cell assembly had reached the desired temperature, the diffusion measurement was initiated by driving the movable cell segment against the mechanical stop to form the aligned capillary diffusion column. After a measured time interval for the isothermal diffusion process, the stop was released and the capillary column sheared by driving the movable section aside until the capillary sections were isolated from each other and the overflow tubes. The diffusion cell was then cooled and removed from the oven.

The capillaries were emptied into the liquid scintillation counting vials. The weight of the amalgam was determined to ascertain that none of the amalgam had been lost during handling. Twenty ml of the nitric acid solution was then pipetted into the vials and the radioactivity of each sample was determined in the liquid scintillation counter. The samples were retained and counted periodically to verify system stability. Total counts greater than 1,000,000 were taken on all samples to reduce counting errors.

CHAPTER V

EXPERIMENTAL RESULTS

Self-diffusion coefficients for the zinc amalgams percent zinc were measured by the modified shear-cell technique at 323, 373, 423, and 473°K. The self-diffusion coefficients were calculated from Equation C-17 using the computer program given in Appendix D. The self-diffusion coefficients and the parameters needed to calculate them are presented in Table I.

The data were fitted to the Arrhenius equation:

$$D = D_o \, e^{-E/RT} \tag{12}$$

where:

D = self-diffusion coefficient, cm^2/sec

R = gas constant, 1.98717 cal/gm-mole °K

T = temperature, °K

D_o = prexponential factor, cm^2/sec

E = activation energy, cal/gm-mole

The self-diffusion coefficients are plotted in Figure 2. The solid straight line represents the Arrhenius equation with the parameters $D_o = 4.6 \times 10^{-4}$ cm^2/sec and E = 1920 cal/gm-mole.

TABLE I

MEASURED SELF-DIFFUSION COEFFICIENTS IN ZINC AMALGAMS

AT 1.440 WEIGHT PERCENT

Temp (^{o}K)	$Dx10^{5}$ (cm^{2}/sec)	Time (sec)	β	$\pm\Delta\beta$	$\pm\Delta Dx10^{5}$ (cm^{2}/sec)
318.2	1.91	32390	.7198	.0014	.02
318.2	1.94	39540	.6860	.0012	.01
317.2	2.01	46449	.6526	.0017	.02
318.2	2.11	36937	.6838	.0017	.02
318.2	2.11	36278	.6807	.0024	.03
317.7	2.16	33975	.6938	.0021	.03
318.7	2.17	38651	.6714	.0024	.03
318.2	2.18	47831	.6315	.0016	.02
314.2	2.54	31703	.6782	.0014	.02
319.8	2.75	56083	.5493	.0022	.03
313.3	2.72	41024	.6139	.0020	.03
316.2	2.91	30355	.6622	.0014	.02
319.6	3.67	50552	.5043	.0015	.02
377.2	2.98	33050	.6477	.0018	.03
379.2	3.12	62759	.4906	.0018	.02
373.2	3.83	31170	.6053	.0022	.04
373.2	4.66	30878	.5650	.0022	.05
373.2	4.83	60833	.3782	.0019	.03
431.2	4.52	29760	.5800	.0019	.04
472.2	4.37	45157	.4891	.0016	.03
472.2	4.88	36919	.5103	.0016	.03
468.2	5.51	31123	.5242	.0019	.04
473.2	5.62	38600	.4599	.0018	.04
471.2	5.89	49502	.3982	.0018	.04
472.2	6.03	47455	.3861	.0017	.04
477.2	6.54	29852	.4917	.0014	.04
471.2	6.76	45167	.3667	.0017	.04

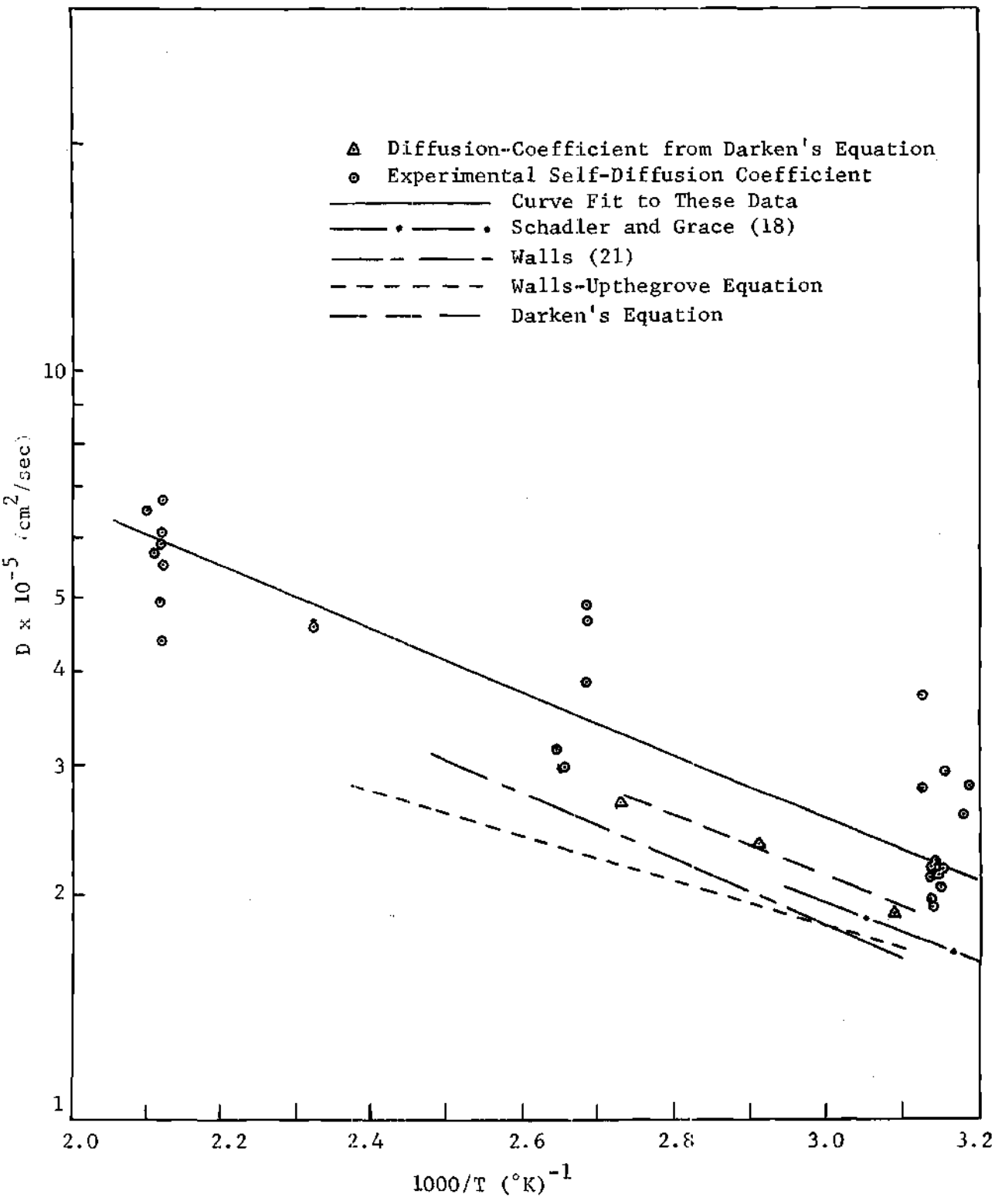

Figure 2. Self-Diffusion and Inter-Diffusion in 1.440 Weight Percent Zinc Amalgams.

CHAPTER VI

DISCUSSION OF RESULTS

The experimental results are discussed in this chapter, including comparisons with existing experimental data and with the correlation proposed by Walls and Upthegrove (38). Using the self-diffusion coefficients of mercury in zinc amalgams published by Schadler and Grace (18) and the self-diffusion coefficients of zinc in zinc amalgams found in this study, the inter-diffusion coefficients of the system were calculated from Darken's equation (23).

Self-diffusion coefficients for 1.440 weight percent zinc in the zinc amalgam are compared to the data of Schadler and Grace (18) in Figure 2. The data of Schadler and Grace were interpolated to obtain values at 1.440 weight percent. Schadler and Grace presented data at 0.103, 0.488, and 1.630 weight percent over the temperature range 285°K to 333°K. They reported a standard deviation of 0.16×10^{-5} cm^2/sec for the 68 determinations at 0.488 weight percent and a standard deviation of 0.13×10^{-5} cm^2/sec for the 52 values of the self-diffusion coefficient at 1.630 weight percent. The self-diffusion coefficients determined in this work are about 30 percent higher than the self-diffusion coefficients measured by Schadler and Grace, but the slopes of the two curve fit lines are in good agreement. However, the pure mercury data of Schadler and Grace is about 30 percent lower than the majority of the reported pure mercury self-diffusion coefficients, including those determined by Broome and Walls (4) who used the modified

shear-cell method. The standard deviation for the self-diffusion coefficients in this work is 0.69 x 10^{-5} cm^2/sec.

Walls (20) data which covered a temperature range from 323°K to 393°K are also plotted in Figure 2. The composition of the amalgam in this work was 4.29 atomic percent zinc. The line shown on Figure 2 was obtained by extrapolating between 3.473 and 5.609 atomic percent zinc amalgam as given by Walls. A curve fit of Wall's data was not made and a standard deviation was not reported.

The major problem encountered in the course of this work was the formation of gas bubbles in the capillaries. Although this problem was not severe at 323°K, it became critical at higher temperatures. Even vacuum degassing the capillaries for several hours at elevated temperatures failed to remove all the gas bubbles. Many runs were made only to discover that the capillaries were not full. In evaluating the results, all of these runs were discarded.

In an attempt to make degassing the capillaries more effective, one set of shear cells was drilled out to a capillary diameter of 2.6 mm. The self-diffusion coefficients determined in these shear cells (listed in Table II in Appendix F) were almost an order of magnitude greater than the coefficients shown in Table I and displayed a great deal more scatter. Edwards et al. (3) concluded that even under favorable conditions, convection effects will be appreciable for experiments conducted with diffusion paths greater than a few millimeters in diameter. The present work supports his conclusion.

Slight variations in $C_2(t)$ or C_o in Equation C-15 also produce very large changes in the diffusion coefficient. As described

previously, a standard nitric acid solution was used to dissolve all the amalgams prior to counting in the liquid scintillation counter. The color of the solutions sometimes varied from water white to a very pale green. The samples were rerun periodically and after correcting for decay the count rate proved to be constant. Equation C-15 gives β as a concentration ratio and the errors due to color cancel out. The errors in the self-diffusion coefficients, due to the random nature of radioactivity, are shown in Table I. The values of $\Delta\beta$ are calculated using Equation C-18 in Appendix C. The error in the diffusion coefficient caused by the random nature of the counts is quite small due to the large number of counts taken on each sample, usually above 1,000,000 counts.

The zinc amalgams were not analyzed for impurities that might occur as a result of dissolving the platinum electrodes or corroding the capillaries. The method of Crenshaw is a standard procedure to prepare amalgams and has been used by several investigators with satisfactory results. Visual inspection showed that the capillaries in the shear cells remained bright and shiny with no pitting occuring. There was no measureable change in the capillary diameter over the course of this project.

The inter-diffusion coefficients were calculated using Equation 11. The values for the activity coefficients were obtained from Walls and Upthegrove (41) at the temperatures 323, 343, and 366°K. The self-diffusion coefficients for zinc were obtained from this work and the self-diffusion coefficients of mercury in zinc amalgams were obtained

from the data of Schadler and Grace (18). The inter-diffusion coefficients of the system determined from the Darken (23) equation are plotted in Figure 1. Sample calculations are shown in Appendix E.

The self-diffusion coefficients were also calculated from the Walls-Upthegrove equation (38) which is presented in the theory section. The density data of Walls (20) from 323°K to 393°K were used to calculate the molar volumes of the amalgams. Walls (20) also presented b values for the various amalgam concentrations. The parameter, γ, was given as 4/3 and the entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) had been determined by fitting kinematic viscosity data. Sample calculations are given in Appendix E and the curve representing the self-diffusion coefficients is shown on Figure 2.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

This work involved the measurement of self-diffusion coefficients for 1.440 weight percent zinc amalgams from 323°K to 473°K at atmospheric pressure. The experimental results from this work are compared to existing data, the Darken equation, and a correlation developed by Walls and Upthegrove. Based on this work, the following conclusions and recommendations are made.

Conclusions

1. Self-diffusion coefficients for a 1.440 weight percent zinc-amalgam from 323°K to 473°K at atmospheric pressure were successfully measured by the modified shear-cell technique developed by Broome and Walls.

2. The self-diffusion coefficients determined in this work agree relatively well with the values measured by Schadler and Grace and by Walls using the capillary-reservoir technique.

3. The self-diffusion coefficients predicted from the Walls-Upthegrove equation are in good agreement with the data taken in this study.

Recommendations

1. More consistent results might be obtained for this system with a well-type scintillation counter, due to the color problems with

liquid scintillation counting.

2. A higher vacuum system would better degas the capillaries and give more consistent results.

APPENDIX A

NOMENCLATURE

A_o, A_n - constants arising from solution to Fick's second law

b - a geometrical parameter which is defined as the ratio of the diffusing particle radius to the interatomic spacing

B - constant in the kinematic viscosity equation, cm^2/sec

D - diffusion coefficients, cm^2/sec

D_A - self-diffusion coefficient of A in Darken's equation, cm^2/sec

D_B - self-diffusion coefficient of B in Darken's equation, cm^2/sec

D_o - prexponetial factor in Arrhenius equation, cm^2/sec

cpm - concentration in radioactive counts per minute

C - concentration

Ci - quantity of radioactive material disintegrating at the rate of 3.7×10^{10} atoms/sec

C_{avg} - average of C_s and C_o at $t = \infty$, cpm

C_f - final capillary concentration in the capillary-reservoir technique, cpm

C_o - initial concentration in the capillary in the capillary-reservoir technique and in the radioactive side of the shear-cell technique, cpm

C_r - reservoir concentration in capillary-reservoir technique, cpm

C_s - non-radioactive capillary concentration in the shear-cell technique, cpm

$C_2(t)$ - average concentration of the radioactive capillary at time, t, in the shear-cell technique, cpm

E - activation energy for the Arrhenius equation, cal/gm-mole

H_i - error in iterative solution to the shear-cell diffusion

equation

ΔH^* - enthalpy of activation for kinematic viscosity, cal/gm-mole

h - Planck's constant, erg/sec

J - diffusion flux, gm-moles/sec cm^2

k - thermal conductivity, cal/sec°K cm

K - Boltzmann's constant, erg/°K

L - length, cm

L_1 - length of non-radioactive capillary in shear-cell system, cm

L_2 - length of radioactive capillary in shear-cell system, cm

M_A - molecular weight of A, gm/gm-mole

M_B - molecular weight of B, gm/gm-mole

N_A - mole fraction of A

N_B - mole fraction of B

N_i - number of radioactive counts

N_o - Avagadro's number, $(gm\text{-}mole)^{-1}$

q - heat flux, cal/sec cm^2

R - gas constant, 1.98717 cal/gm-mole °K

ΔS^* - entropy of activation for kinematic viscosity, cal/gm-mole °K

t - time, sec

T - temperature, °K

v - velocity, cm/sec

V - molar volume, cm^3/gm-mole

X - distance, cm

Greek Symbols

β - experimentally determined concentration ratio in modified shear-cell technique

$\Delta\beta$ - error in β due to random nature of radioactive counting

γ - a configurational parameter dependent only upon the coordination number of the liquid

γ_B - activity coefficient of B

θ - parameter containing D in solution to Fick's second law for capillary-reservoir and shear-cell technique

λ_n - constant arising from solution to Fick's second law

μ - absolute viscosity, gm/cm sec

τ - shear stress, dynes/cm^2

ψ - experimentally determined concentration ratio in capillary-reservoir technique

Nomenclature for Computer Program

"Calculation of Self-Diffusion Coefficients"

DB - $\Delta\beta$

NRUN - RUN NUMBER

T - TIME OF RUN, SEC

SL1 - L_1, CM

SL2 - L_2, CM

C0 - C_0, CPM

CS - C_S, CPM

C2T - $C_2(T)$, CPM

TEMP - T, °K

APPENDIX B

RADIOACTIVE MATERIALS SPECIFICATIONS

Item	Value
Isotope	Zinc-65
Half-Life	243.7 days
Chemical form	$ZnCl_2$ in HCl
Acidity	.5N HCl
Specific Activity	3.35 Ci/mg
Concentration	30.2 m Ci/ml
Volume	.165 ml
Radiometric purity	>99%
Total solids	9.0 mg/ml
Modes of Decay and Energy in MEV	Electron Capture, Position, .329 Gamma, 1.1155

APPENDIX C

MATHEMATICAL ANALYSIS OF MODIFIED SHEAR-CELL DIFFUSION

The mathematical analysis for diffusion in the finite-capillary geometry of the modified shear-cell is given by Walls (1). Three assumptions are made: 1) the diffusion flux is described by Fick's first law, 2) the diffusion coefficient is independent of concentration, and 3) the volume change on mixing is zero.

Fick's second law is solved by separating the variables and using the following boundary and initial conditions:

$$\frac{\partial C(-L_1,t)}{\partial X} = 0 \qquad \text{(C-1)}$$

$$\frac{\partial C(L_2,t)}{\partial X} = 0 \qquad \text{(C-2)}$$

$$C(X,0) = C_s \qquad -L < X < 0 \qquad \text{(C-3)}$$

$$C(X,0) = C_o \qquad 0 < X < L_2 \qquad \text{(C-4)}$$

$$C(X,\infty) = C_{avg} \qquad \text{(C-5)}$$

where:

C = concentration, cpm

L_1 = non-radioactive capillary length, cm

L_2 = radioactive capillary length, cm

t = time, sec

C_s = initial concentration on the non-radioactive side, cpm

C_o = initial concentration on the radioactive side, cpm

C_{avg} = average of C_s and C_o at $t = \infty$, cpm

X = distance down capillaries, cm

The general solution is:

$$C(X,t) = A_o + \sum_{n=1}^{\infty} A_n e^{-\lambda_n^2 Dt} \cos \lambda_n (X-L_2) \qquad (C\text{-}6)$$

where:

$$\lambda_n \equiv \frac{n\pi}{L_1 + L_2} \qquad (C\text{-}7)$$

$$A_o = \frac{1}{L_1 + L_2} \int_{-L_1}^{L_2} C(X,0)\, dX \qquad (C\text{-}8)$$

$$A_n = \frac{2}{L_1 + L_2} \int_{-L_1}^{L_2} C(X,0) \cos \lambda_n (X - L_2)\, dX \qquad (C\text{-}9)$$

By substituting Equations C-3 and C-4 into Equation C-8, the following is obtained:

$$A_o = \frac{C_s L_1 + C_o L_2}{L_1 + L_2} \qquad (C\text{-}10)$$

Using the conditions of orthogonality, Equation C-9 is integrated to give:

$$A_n = (C_o - C_s)\left(\frac{2}{L_1 + L_2}\right)\left(\frac{1}{\lambda_n}\right) \sin \lambda_n L_2 \qquad (C\text{-}11)$$

Integrating the general solution over the length of the radioactive capillary in Equation C-6 and dividing by L_2 yields:

$$C_2(t) = \frac{1}{L_2} \int_o^{L_2} C(X,t)\, dX \qquad (C\text{-}12)$$

The average concentration in the radioactive capillary, when expressed as a function of time is:

$$C_2(t) = A_o + \frac{1}{L_2} \sum_{n=1}^{\infty} \frac{1}{\lambda_n} A_n e^{-\lambda_n^2 Dt} \sin(\lambda_n L_2) \qquad \text{(C-13)}$$

Inserting the values for A_o and A_n into Equation C-13 gives:

$$C_2(t) = \frac{C_s L_1 + C_o L_2}{L_1 + L_2} + \frac{2(C_o - C_s)(L_1+L_2)}{L_2 \pi^2} \sum_{n=1}^{\infty} \left[\frac{1}{n} \sin \frac{n\pi L_2}{L_1+L_2}\right]^2 x$$

$$\left[\exp - \left[\frac{n\pi}{L_1+L_2}\right]^2 Dt\right] \qquad \text{(C-14)}$$

Using the definitions:

$$\beta = 2\left[\frac{C_2(t)\ (L_1+L_2) - C_s L_1 - C_o L_2}{(C_o - C_s)(L_1+L_2)}\right] \qquad \text{(C-15)}$$

and:

$$\theta = \frac{Dt}{(L_1+L_2)^2} \qquad \text{(C-16)}$$

Equation C-14 becomes:

$$\beta = \frac{4(L_1+L_2)}{\pi^2 L_2} \sum_{n=1}^{\infty} \left[\frac{1}{n} \sin \frac{n\pi L_2}{L_1+L_2}\right]^2 \exp - (n\pi)^2 \theta \qquad \text{(C-17)}$$

Equation C-17 is the solution to Fick's second law for the modified shear-cell.

The value β is the experimentally determined concentration ratio. The random error in β can be calculated in terms of the individual random counting error associated with each radioactivity measurement as:

$$\Delta\beta = \frac{2}{C_o - C_s} \left\{(\Delta C_2(t))^2 + \left[\frac{C_2(t) - C_s}{C_o - C_s}\right]^2 (\Delta C_o)^2 + \left[\frac{C_o - C_2(t)}{C_o - C_s}\right]^2 x\right.$$

$$(\Delta C_s)^2\}^{1/2} \qquad \text{(C-18)}$$

where ΔC_i, the error in the individual count rate, is expressed in terms of the total number of counts, N_i, as

$$\Delta C_i = C_i(N_i)^{-1/2} \qquad \text{(C-19)}$$

APPENDIX D

COMPUTER PROGRAM FOR CALCULATION OF DIFFUSION COEFFICIENTS AND INSTRUCTIONS FOR ITS USE

The iterative scheme used to calculate θ and the self-diffusion coefficient in Equation C-17 involves calculating a θ_1 value from the first term approximation of the experimentally derived β value. This θ_1 value is then used to evaluate the series solution and the difference between the computed value $\bar{\beta}$ and β is given as:

$$H_i = \frac{4}{\pi^2}\frac{L_1+L_2}{L_2}\sum_{n=0}^{N}\left[\frac{1}{n}\sin\frac{n\pi L_2}{L_1+L_2}\right]^2 \exp[-(n\pi)^2\theta]-\beta = \bar{\beta} - \beta \qquad \text{(D-1)}$$

Using the Newton-Raphson method, θ_i is iterated to determine that value of θ_i which reduces H_i to some specified limit; i.e.:

$$\theta_{i+1} = \theta_i - H(\theta_i)/H'(\theta_i) \qquad \text{(D-2)}$$

in which the subscript i denotes the number of iterations. It was found that five iterations, N = 5 in equation D-1, gave sufficient accuracy for θ_i, and to calculate D, the value of H_i was less than .000000001.

The program used to calculate the diffusion coefficient is shown in Figure 3. For run number 81 the following data were collected:

DB = .0022 (calculated from Equation C-18)

NRUN = 81

T = 56083 sec

SL1 = 3.10 cm

SL2 = 3.01 cm

C0 = 13479 cpm

C2T = 10347 cpm

CS = 20 cpm

TEMP = 319.8°K

The program, "Calculation of Self-Diffusion Coefficients", calculated these values:

NRUN	T	SL1	SL2	C0	CS	C2T	TEMP	1000/T	D*10-5	BETA
81	56083	3.10	3.01	13479	20.0	10347	319.8	2.651	2.750	.5493

D-BETA	THETA
.0022	.04131

The program must be run twice to calculate the change in the self-diffusion coefficient shown in Table I. Positive and negative values of DB are read into the program and a card is inserted setting BETA equal to BETA plus DB.

```
C
C                    CALCULATION OF SELF-DIFFUSION COEFFICIENTS
C
      DIMENSION P(20)
      PI = 3.14159265
      WRITE(6,10)
    1 M = 0
      READ(5,20,END=5)DB,NRUN,T,SL1,SL2,CO,CS,C2T,TEMP
      RL = SL2/(SL1 + SL2)
      BET1 = C2T * (SL1 +SL2) -CS*SL1 - CO*SL2
      BET2 = ((CO - CS) * (SL1 + SL2))
      BETA = 2.0*(BET1/BET2)
      THETA = -(1/(PI**2))*ALOG((PI*PI*BETA*RL)/(4.*(SIN(PI*RL)**2)))
    2 HP = 0
      H = 0
      DO 3 N = 1,5
      P(N) = ((SIN(N*PI*RL))**2)*EXP(-((N*PI)**2)*THETA)
      HP = HP + P(N)
    3 H = H + P(N)/(N*N*PI*PI)
      HP = -4.*HP/RL
      H = 4.*H/RL - BETA
      THETA = THETA - H/HP
      M = M + 1
      IF(M.GT.10) GO TO 4
      HA = ABS(H)
      IF (HA.GT.0.000000001) GO TO 2
    4 CONTINUE
      D = 10000.* (SL1 + SL2)**2/T*THETA
      TEM = 1000./TEMP
      WRITE(6,30)NRUN,T,SL1,SL2,CO,CS,C2T,TEMP,TEM,D,BETA,DB,THETA
      GO TO 1
    5 CONTINUE
      STOP
   10 FORMAT(1H1,3HRUN,5X,1HT,7X,3HSL1,4X,3HSL2,5X,2HCO,6X,2HCS,5X,3HC2T
     1,6X,4HTEMP,2X,6H1000/T,4X,6H*10-5,4X,4HBETA,4X,6HD-BETA,4X,5HTHET
     2A/)
   20 FORMAT(F8.0,I2,7F10.0)
   30 FORMAT(1X,I4,F9.0,2F7.2,F9.0,F7.1,F9.0,F8.1,F8.3,3F9.4,F10.5)
      END
```

Figure 3. Computer Program, "Calculation of Self-Diffusion Coefficients"

APPENDIX E

SAMPLE CALCULATIONS

Inter-Diffusion Coefficient From Darken's Equations

At 323°K , the first term of Darken's Equation is obtained from the work of Schadler and Grace (18) and this work; the values used to calculate this term are:

$$D_B(Zn) = 4.6 \times 10^{-4} \exp\ (-1920/1.98717 \times 323.15)$$

$$= 2.3 \times 10^{-5}\ cm^2/sec$$

$$D_A(Hg) = 1.52 \times 10^{-4} \exp\ (-1605/1.98717 \times 323.15)$$

$$= 1.25 \times 10^{-5}\ cm^2/sec$$

$$N_A(Hg) = .9571$$

$$N_B(Zn) = .0429$$

The first term is:

$$(N_A D_B + N_B D_A) = 2.26 \times 10^{-5}\ cm^2/sec$$

From the data of Walls and Upthegrove (41) at 323°K, the term containing the activity coefficient can be calculated as:

$$\frac{\partial\ \ell n\ \gamma_B}{\partial\ N_B} = \frac{(\ell n\ \gamma_B)_2 - (\ell n\ \gamma_B)_1}{(N_B)_2 - (N_B)_1}$$

$$= \frac{\ell n\ 12.590 - \ell n\ 13.107}{.04464 - .03447}$$

$$= -3.957$$

Therefore, the second term is:

$$(1 + N_B \frac{\partial \ln \gamma_B}{\partial N_B}) = .83$$

and the diffusion coefficient is:

$$D = 2.26 \times 10^{-5} \ (.83)$$
$$= 1.88 \times 10^{-5} \ cm^2/sec$$

Self-Diffusion Coefficient from the Walls-Upthegrove Equation

The Walls-Upthegrove equation may be expressed as:

$$D = \frac{KT \ \gamma^{1/3}}{2\pi h \ b \ (2b+1)} \left(\frac{V}{N_o}\right)^{2/3} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (12)$$

The parameter, γ, as given by Walls and Upthegrove (38), is 4/3. The value of b is .443 and is obtained from the work of Walls (20). The volume fraction, $\Phi(Z_n)$, calculated from standard density data, is .0271. Walls (20) has fitted viscosity data to obtain the expression:

$$\Delta H^*(Zn\text{-}Hg) = 2210 \ \Phi(Zn) + 559 \qquad (E\text{-}1)$$

this gives:

$$\Delta H^*(Zn\text{-}Hg) = 2210 \ (.0271) + 559$$
$$= 618.84 \ cal/mole$$

and:

$$B(Zn\text{-}Hg) = \frac{4.396 + 3.736\Phi(Zn)}{10^4} \qquad (E\text{-}2)$$
$$= 4.497 \times 10^{-4}$$

The entropy of activation is calculated by the following equation from the work of Walls (20):

$$\frac{\exp\left(\frac{\Delta S^*}{R}\right)}{h} = \frac{N_o}{B(N_A M_A + N_B M_B)} \qquad \text{(E-3)}$$

$$= \frac{6.02252 \times 10^{23}}{4.497 \times 10^{-4}(194.7872)}$$

$$= 6.875 \times 10^{24}$$

The enthalpy of activation is:

$$\exp(-\Delta H^*/RT) = \exp(-618.8/1.986 \times 343.35)$$

$$= .4037$$

At 343.35°K, the density data of Walls (20) is used to calculate the molar volume:

$$V = \left(\frac{13.30 \text{ gm/cc}}{194.7872 \text{ gm/gm-mole}}\right)^{-1}$$

$$= 14.65 \text{ cc/gm-mole}$$

Therefore, at 343.35°K the self-diffusion coefficient is:

$$D = \frac{(1.3805 \times 10^{-16})(343.35)}{2\pi} \times \frac{1}{.443(2(.443)+1)} \times \left(\frac{4}{3}\right)^{1/3}$$

$$\times \left(\frac{14.65}{6.02252 \times 10^{23}}\right)^{2/3} \times 6.875 \times 10^{24} \times .4037$$

$$= 1.91 \times 10^{-5} \text{ cm}^2/\text{sec}$$

APPENDIX F

TABLE II

MEASURED SELF-DIFFUSION COEFFICIENTS IN ZINC AMALGAMS AT 1.440 WEIGHT PERCENT ZINC FOR THE 2.6 MM DIAMETER CAPILLARIES

$Dx10^5$ (cm^2/sec)	$1000/T$ $(^oK)^{-1}$	T (^oK)
2.76	3.16	316.2
3.17	3.16	317.2
3.30	3.15	317.2
4.29	3.16	316.0
6.27	3.18	314.0
9.16	3.17	315.2
14.19	3.10	322.8
20.68	3.13	319.4
3.15	2.69	371.2
4.05	2.69	371.2
5.41	2.68	373.2
5.70	2.69	372.2
7.91	2.68	373.0
13.20	2.68	373.0
13.56	2.69	372.2
16.79	2.68	373.2
20.12	2.68	373.2
12.48	2.39	419.2
17.38	2.38	420.2
19.68	2.37	422.2
28.21	2.37	427.2
34.74	2.37	421.2

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